Review of the Proposed Basin Plan Amendment to Adopt Total Maximum Daily Loads (TMDLs) for Toxicity and Pesticides in the Santa Maria Watershed

Reviewer: Jeffrey Jenkins, Ph.D.
Department of Environmental and Molecular Toxicology
Oregon State University

It is my understanding that according to the Cal/EPA External Peer Review Guidelines all important scientific underpinnings of the proposed science-based rule – Basin Plan Amendment to Adopt TMDLs for Toxicity and Pesticides in the Santa Maria Watershed – must be submitted for external peer review, and that the underpinnings would include all publications (including conference proceedings), reports, and raw data upon which the proposal is based. I understand that it is the reviewer's responsibility is to determine whether the scientific portion of the proposed rule is based upon sound scientific knowledge, methods, and practices. I also recognize that the Cal/EPA External Peer Review Guidelines note that there are circumstances where external peer review of supporting scientific documents is not required, such as "A particular work product that has been peer reviewed with a known record by a recognized expert or expert body."

In the Central Coast Regional Water Quality Control Board memo from Christopher Rose dated June 28, 2012, 5 discrete TMDL elements of the proposed regulatory action have been identified for review: 1) Numeric Targets, 2) Source Analysis, 3) TMDLs and Allocations, 4) Implementation, 5) Monitoring. For each element, the primary issue(s) that constitute the scientific basis of the proposed regulatory action have been identified. I have reviewed the final project report (August 2012) in its entirety, as well as most of the supporting documentation. Given my areas of expertise, my review will focus on the primary scientific issues for elements 1) and 2); where there is overlap, I will also address certain aspects of the remaining elements.

1) Numeric Targets

The primary scientific issue is the scientific basis for the assignment of numeric targets for specific pesticides addressed in the TMDL.

In the Central Coast Regional Water Quality Control Board memo from Christopher Rose dated June 28, 2012, Attachment Five – Water, Sediment, and Fish Tissue Chemistry Numeric Targets – lists water chemistry numerical targets for the organophosphate (OP) insecticides chlorpyrifos, diazinon, and malathion; the synthetic pyrethroid insecticides bifenthrin, cyfluthrin, and λ-cyhalothrin; and the legacy organochlorine (OC) insecticides DDT, DDD, DDE, chlordane, dieldrin, and toxaphene.

Sediment chemistry numerical targets are provided for the OP chlorpyrifos; the synthetic pyrethroids bifenthrin, cyfluthrin, λ-cyhalothrin, cypermethrin, permethrin, and esfenvalerate; and the legacy OCs DDT, DDD, DDE, chlordane, dieldrin, toxaphene, and endrin.

Fish tissue numeric targets are provided for the legacy OCs – chlordane, DDTs, dieldrin, and toxaphene.

The numeric targets in Attachment Five are listed as concentrations (with units) for a given endpoint (CMC, CCC, etc.), along with a reference for that supports the derivation of the numerical target.

The water chemistry numeric targets for the OPs chlorpyrifos and diazinon have been previously derived by the California Department of Fish and Game (CDFG 2000), and further evaluated in the California Regional Water Quality Control Board Central Coast Region project report "TMDLs for Chlorpyrifos and Diazinon in the Lower Salinas River Watershed" (CCRWQCB 2011). These numeric targets are considered sufficiently “peer reviewed with a known record by a recognized expert or expert body.” Similarly, as the legacy OC water chemistry numeric targets are derived from the concentration established by the U.S. Environmental Protection Agency (EPA 2000), no further review will be provided. For the sediment and fish tissue chemistry no additional peer review will be conducted for the legacy OCs as references (WDOH, 1995 and OEHHA, 2008) for the numerical targets are deemed sufficiently peer reviewed.

For the pesticides – the OP malathion and the synthetic pyrethroids – evaluation of the scientific basis for the assignment of numeric targets will largely rely on the review of methodologies conducted by TenBrook and Tjeerdema (2006), and subsequent derivation and application of the UC-Davis methodology for specific pesticides (TenBrook et al., 2009), as these reports are considered current, highly relevant, and comprehensive.

The UC-Davis methodology used as the basis for the assignment of acute and chronic numeric targets contains the following elements in a step by step format:

- Guidance for collection, evaluation, and reduction of data;
- A species sensitivity distribution (SSD) method to derive criteria when data are available for five representative taxa - 1) a warm water fish, 2) a fish in the family Salmonidae, 3) a planktonic crustacean – Ceriodaphnia, Daphnia, or Simocephalus, 4) a benthic crustacean, and 5) an insect (aquatic exposure).
- An assessment factor (AF) method to derive acute criteria when fewer than five acute toxicity data are available;
- A default acute-to-chronic ratio (ACR) to derive chronic criteria when fewer than five chronic data are available;
- Methods for assessing bioavailability;
- Methods for assessing compliance in cases of mixtures of chemicals with similar modes of toxic action and for mixtures that exhibit non-additive toxicity;
- Methods for quantifying relationships between toxicity and water quality parameters, such as pH and temperature;
- Techniques for assessing whether derived criteria might harm particularly sensitive species, lead to bioaccumulation, harm ecosystems, harm threatened and endangered species, or lead to unacceptable levels of pesticides in other environmental compartments;
- A template for describing final criteria in terms of magnitude, duration and frequency

This methodology defines a pesticide as "1) any substance or mixture of substances that is intended to be used for defoliating plants, regulating plant growth, or for preventing, destroying, repelling, or mitigating any pest, which may infest or be detrimental to vegetation, man, animals, or households, or be present in any agricultural or nonagricultural environment whatsoever, or 2) any spray adjuvant, or 3) any breakdown products of these materials that threaten beneficial uses."

The methodology prescribes appropriate endpoints for criteria derivation as those that measure survival, growth, or reproductive effects. Surrogates (i.e., LC_{50}, EC_{50}, NOEC, LOEC, MATC) may be used if those endpoints have been linked to effects on survival, growth, or reproductive effects.

Review of the scientific basis for the assignment of numeric targets for malathion

The selected malathion water chemistry numerical target was derived using the UC-Davis methodology as described in Faria et al., 2010. The UC-Davis methodology derived numeric targets were used as there are no Clean Water Act (CWA) National Standards for malathion. However, for comparison, using the same data set, the malathion numerical targets were derived using National Standard methodology (USEPA 1985).

As acute data for the all of the 5 representative taxa were not available for malathion, the SSD method could not be used. Instead the AF method was used to estimate the median 5th percentile value (acute value) of the SSD, which was subsequently used to calculate the acute criterion. Employing the AF method, using LC_{50} or EC_{50} data for 4 of the 5 representative taxa, resulted in an acute criterion = 0.17 ug/L. As the AF method may be considered more conservative[1] than the SSD method, in the absence of a complete data set, use of the AF method is considered appropriately protective of aquatic life.

As chronic data for only 3 of the 5 representative taxa were available for malathion, the ACR method was used to calculate the chronic criterion by pairing chronic toxicity values (MATC) with an appropriate corresponding acute toxicity value (LC_{50}) in order to calculate an ACR; resulting in the ACR-derived chronic criterion = 0.028 ug/L. As with the acute criterion derived from the AF method, in the absence of a complete data set, the ACR method is considered conservative and appropriately protective of aquatic life.

Table 1. USEPA OPP aquatic toxicity reference values for malathion

Exposure Scenario	Species	Exposure Duration	Toxicity Reference Value
Freshwater Fish			
Acute	Bluegill sunfish	69 hr	LC_{50} = 30 ug/L
Chronic	Rainbow trout	97 day	NOEC 21 ug/L
Freshwater Invertebrates			
Acute	Water flea, *Daphnia magna*	48 hr	EC_{50} = 1.0 ug/L
Chronic	Water flea, *Daphnia magna*	21 day	NOEC = 0.06 ug/L

Malathion products are registered for use in California by the USEPA Office of Pesticide Programs (OPP) in partnership with California EPA Department of Pesticide Regulation. The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) requires that pesticides registered by EPA do not pose

[1] Critical to this approach is the use of sufficiently conservative procedures to minimize false negative outcomes – i.e., for every statistical comparison, there is always a defined probability that a difference will not be designated as significant, when in fact it is (Type I error or false negative when there is a null hypothesis of some adverse effect).

"unreasonable adverse effects on the environment"[2]. EPA periodically evaluates pesticide use practices to determine if they meet this requirement. The most recent Reregistration Eligibility Decision (RED) for malathion was published in 2006 (EPA 738-R-06-030). In this decision EPA compared edge-of-field surface water expected environmental concentrations (EECs) with aquatic life levels of concern (LOC). USEPA OPP aquatic toxicity reference values for malathion used in this analysis are shown in Table 1.

Using the risk quotient (RQ) method, EECs are divided by the malathion aquatic toxicity reference values (TRV). In determining LOCs, for acute exposures RQ=0.5; for chronic exposures RQ=1, and for endangered species protection RQ=0.05. If LOCs are expected to be exceeded then EPA may choose to cancel a registered use or require additional mitigation measures. Using the malathion TRVs for freshwater invertebrates and the associated RQs, the acute LOC is 0.5 ug/L and the chronic LOC is 0.06 ug/L. These levels are roughly 2X the proposed acute and chronic numeric targets for malathion, suggesting that additional mitigation measures may be required to reduce surface water loading associated with labeled malathion use practices.

In 2008 the National Marine Fisheries Service issued a biological opinion[3], under the authority of section 7(a)(2) of the Endangered Species Act (ESA), on the effects of the USEPA registered pesticide products containing the active ingredients chlorpyrifos, diazinon, and malathion on endangered and threatened salmonid species, and critical habitat that has been designated for those species. In that opinion, risks to salmonid evolutionary significant units (ESUs), including steelhead whose critical habitat includes the South-Central California Coast, associated with exposure to malathion where evaluated. Effect concentrations were determined for salmon swimming behavior, fish reproduction and growth, salmon survival, and prey survival. Effect concentrations were lowest for prey survival, ~0.2 ug/L. The proposed malathion acute criterion of 0.17 ug/L is consistent with this finding.

Conspicuously absent from this analysis is consideration of any malathion breakdown products that threaten beneficial uses. It is widely known that the organophosphate insecticides, including malathion, are transformed in the environment to the more toxic oxon degradate. In addition, research suggests that organophosphate oxon degradates are more stable in the atmosphere than the parent compound. Studies investigating the airborne transport of organophosphate pesticides from the central valley of California to the Sierra Nevada Mountains often found levels of the oxon degradate at higher levels than the parent compound.[4,5] Dry and wet deposition can result in the occurrence of both the parent organophosphates and oxon degradates in surface waters[6].

Consequently, for water bodies currently listed as impaired for water column toxicity and malathion detections, additional monitoring should include malathion oxon.

---

[2] FIFRA section 2(bb) defines "unreasonable adverse effects on the environment" to mean, in part, "any unreasonable risk to man or the environment, taking into account the economic, social, and environmental costs and benefits of the use of any pesticide...."(http://www.epa.gov/pesticides/health/risk-benefit.htm)

[3] http://www.nmfs.noaa.gov/pr/pdfs/pesticide_biop.pdf

[4] Zabik, J. M., and J. N. Seiber. 1993. Atmospheric transport of organophosphate pesticides from California's Central Valley to the Sierra Nevada mountains. Journal of Environmental Quality **22**:80-90.

[5] Aston, L. S. and J. N. Seiber. 1997. The fate of airborne organophosphate pesticides transported to the Sierra Nevada mountains in summer. Journal of Environmental Quality **26**:1483-1492.

[6] McConnell, L. L., J. S. LeNoir, S. Datta, and J. N. Seiber. 1998. Wet deposition of current-use pesticides in the Sierra Nevada mountain range, California, USA. Environmental Toxicology and Chemistry **17**:1908-1916.

Review of the scientific basis for the assignment of numeric targets for the synthetic pyrethroids: bifenthrin, cyfluthrin, λ-cyhalothrin, cypermethrin, esfenvalerate, and Permithrin

The scientific basis for the assignment of water chemistry numeric targets for synthetic pyrethroids bifenthrin, λ-cyhalothrin, and cyfluthrin are contained in the water quality criteria Reports, prepared for the Central Valley Regional Water Quality Control Board, which derive acute and chronic water quality criteria using the UC-Davis methodology.

Bifenthrin

The acute criterion for bifenthrin was derived using the SSD method as at least five acceptable acute toxicity values were available and fulfilled the five taxa requirements of the SSD method. The resulting acute criterion, based on the median 5^{th} percentile value, is 0.004 ug/L. This value is considered acceptable for its intended purpose.

Details of the application of the SSD method are as follows:

"The log-logistic SSD procedure (section 3-3.2.2, TenBrook et al. 2009a) was used for the acute criterion calculation because there were not more than eight acceptable acute toxicity values available in the bifenthrin data set (Table 2). The log-logistic SSD procedure was used to derive 5th percentile values (median and lower 95% confidence limit), as well as 1st percentile values (median and lower 95% confidence limit). The median 5th percentile value is recommended for use in criteria derivation by the methodology because it is the most robust of the distributional estimates (section 3-3.TenBrook et al. 2009a). Comparing the median estimate to the lower 95% confidence limit of the 5th percentile values, it can be seen that the first significant figures of the two values are different (0.00803 vs. 0.000391 µg/L). Because there is uncertainty in the first significant digit, the final criterion will be reported with one significant digit (section 3-3.2.6, TenBrook et al. 2009a).

The ETX 1.3 Software program (Aldenberg 1993) was used to fit the log-logistic distribution to the data set, which is plotted with the acute values in Figure 2. This distribution provided a satisfactory fit (see Appendix A) according to the fit test described in section 3-3.2.4 of TenBrook et al. (2009a). No significant lack of fit was found ($\chi 22n = 0.2417$) using the fit test based on cross validation and Fisher's combined test (section 3-3.2.4, TenBrook et al. 2009a), indicating that the data set is valid for criteria derivation."

This approach applies statistical rigor to all available toxicity values that meet data quality criteria, and is among the most robust evaluations of this type currently employed for regulatory purposes worldwide; this approach has the potential to greatly reduce uncertainty in estimating no-effect exposure levels by reducing the probability of both Type I error or false negative when there is a null hypothesis of some adverse effect, and Type II error or false positive; failure to reject the potentially false null hypothesis, i.e., no effect).

As chronic toxicity values from fewer than five different families were available the ACR procedure was used to calculate the bifenthrin chronic criterion. Because an ACR could not be calculated with the available data, the chronic criterion was calculated with the default ACR value of 12.4 = 0.0006 ug/L. Use of the default ACR value is considered conservative and appropriately protective of aquatic life.

λ-cyhalothrin

For λ-cyhalothrin The Burr Type III SSD procedure was used for the acute criterion calculation because more than eight acceptable acute toxicity values were available in the λ-cyhalothrin data set. This procedure, roughly equivalent to the CWA National Standard methodology, the acute criteria=0.001 ug/L is based on the median 5th percentile acute value. This value is considered acceptable for its intended purpose.

As chronic data for only 3 of the 5 representative taxa (including a saltwater species) were available for λ-cyhalothrin, the ACR method was used to calculate the chronic criterion by pairing chronic toxicity values (MATC) with an appropriate corresponding acute toxicity value (LC_{50}) in order to calculate an ACR; resulting in the ACR-derived chronic criterion = 0.0005 ug/L. This value is considered conservative and appropriately protective of aquatic life.

Cyfluthrin

The acute criteria for cyfluthrin was derived using the SSD method as at least five acceptable acute toxicity values were available and fulfilled the five taxa requirements of the SSD. The resulting acute criterion= 0.002 ug/L, based on the median 5th percentile acute value. However, further "sensitivity analysis" determined that this acute criterion is not protective of the sensitive species H. azteca. This determination was based on comparing the result of the SSD analysis – the median 5th percentile acute value – to the lowest acute value for H. azteca. Consequently the median 1st percentile estimate was used to derive the acute and chronic criteria. Use of this less reliable acute value estimate is inconsistent with the derivation of other acute and chronic criteria for which there is sufficient data to use the SSD approach. Given the premise for use of the SSD approach in the UC-Davis Methodology – a robust statistical analysis using all of the available toxicity values that meet data quality criteria – it seems arbitrary to use the median 1st percentile estimate for the sole purpose of deriving a toxicity value that is less than the H. azteca lowest acute value, a single value of unknown significance. If a goal of the SSD approach is to reduce the probability of both Type I and Type II error in estimating the acute value, use of the median 5th percentile acute value is consistent with other assessments and appropriate for its intended purpose, regardless of whether the result is greater than an independent acute value of unknown significance.

Alternatively, if H. azteca is significantly more sensitive than taxa required for use of the SSD approach in the UC-Davis methodology, and is ultimately the driver in determining criteria, then it should be included as a required species for SSD analysis. Otherwise, the statistical power that is derived from the SSD approach may not be appropriate for determination of water quality criteria for some contaminants.

The scientific basis for the assignment of sediment chemistry numeric targets for the synthetic pyrethroids

The scientific basis for the assignment of sediment chemistry numeric targets for the synthetic pyrethroids bifenthrin, cyfluthrin, λ-cyhalothrin, esfenvalerate, and permithrin is contained in the publication by Amweg and Weston (2005)[7]. The scientific basis for the assignment of sediment

[7] Amweg EL, Weston DP, Ureda NM. 2005. Use and toxicity of pyrethroid pesticides in the Central Valley, California, USA. Environ Toxicol Chem 24:966–972; Correction: 24:1300–1301.

chemistry numeric target for cypermethrin is contained in the publication by Maund et al. (2002)[8]. The scientific basis for the assignment of sediment chemistry numeric targets for the organophosphate chlorpyrifos is contained in the publication Amweg and Weston (2007)[9].

Relying on a single study to derive CWA criteria is not the preferred approach. In addition to the paucity of data that may be derived from a single studies, of concern is that research studies whose specific aim(s) are not designed to meet regulatory needs, may not be adequate to provide the scientific basis for the assignment of numeric targets. Sufficient data to allow the use of a "weight of the evidence" approach, such as described in the UC-Davis Water Quality Reports prepared for the Central Valley Regional Water Quality Control Board, is generally preferred by risk assessors and best serves stakeholders. In addition, a common general criticism is often studies are not conducted according to Good Laboratory Practice (GLP), part of the testing guidelines developed by regulators around the world, outlining basic standards for equipment calibration and the storage of raw data. In general, when called on by state and federal regulators to test the safety of a substance, the chemical industry has relied on private labs to carry out studies using GLP; academic researchers rarely conduct such studies. Consequently, while the studies listed above employ the appropriate EPA methods for sediment toxicity[10], I suspect that the research conducted by Maund et al., (2002) was conducted under GLPs, but not the research of Amweg and Weston (2005, 2007). However, in their deliberations about protecting water quality, state and federal agencies are expected to examine all the evidence, GLP or not.

Considering the concerns described above, in critiquing these studies for suitability as scientific basis for the assignment of sediment chemistry numeric targets, I provide the following:

While expressing the numeric target as a value normalized for the organic carbon (ug/g o. c.) is useful in addressing bioavailability, this approach introduces the potential for significant variability depending on how the organic carbon (OC), as a surrogate for organic matter, is considered. For example, in Maund et al., (2002) they state that "Predictions of aqueous concentrations at the LC_{50} in sediments (based on Koc) compared well to each other and to effect concentrations from studies in water alone, suggesting that equilibrium partitioning theory could be used reasonably to predict and normalize the toxicity of cypermethrin across sediments of differing OC content." However they go on to state that "Theoretically, Koc should be a constant for a particular chemical, that is, an increase in OC content should lead to a direct increase in adsorption. However, adsorption probably also is affected by the physical nature of the OC present in the sediment and the surface area available for adsorption (the latter being a function of particle size distribution within the soils). Organic carbon that is present in small, often cominuted particles or coating the surface of mineral particles is likely to present a greater potential for adsorption than larger intact particles of OC, because of increased surface area." However, the methods of analyzing for OC content generally do not take surface area into account, because OC is digested from the sediment in its entirety.

The sorption of a particular pesticide to a soil is measured in a laboratory by mixing water, pesticide, and soil. After equilibrium has been reached, the amount of pesticide remaining in solution is measured. The

[8] Maund, S.J., Hamer, M.J., Lane, M.C.G., Farrelly, E., Rapley, J.H., Goggin, U.M., Gentle, W.E., 2002. Partitioning, bioavailability, and toxicity of the pyrethroid insecticide cypermethrin in sediments. Environ Toxicol Chem 21, 9-15.
[9] Amweg, E.L., Weston, D.P., 2007. Whole-sediment toxicity identification evaluation tools for pyrethroid insecticides: I. Piperonyl butoxide addition. Environmental Toxicology and Chemistry 26, 2389-2396.
[10] U.S. Environmental Protection Agency. 2000. Methods for measuring the toxicity and bioaccumulation of sediment-associated contaminants with freshwater invertebrates, 2nd ed. EPA/600/R-99/064. Washington, DC.

concentration of pesticide sorbed to the soil in the mixture is divided by the pesticide concentration still in solution. This yields the distribution coefficient, Kd. A low distribution coefficient indicates that more of the pesticide is in solution; a higher value indicates that the pesticide is more strongly sorbed to soil. The Kd is soil and pesticide specific; for a given pesticide the Kd is largely dependent on the soil's clay content and the type of clay – which determines surface area, as well as the organic matter attached to the clay surface. The sorption coefficient (Koc) is used to compare the relative sorption of pesticides. Koc is the distribution coefficient Kd divided by the amount of organic carbon in the soil (soils are tested for organic carbon – soil organic carbon is directly proportional to soil organic matter, which is primarily responsible for a soil's sorption properties.) While use of Koc allows a reasonable comparison of pesticides for their sorption to soil and sediment, the variation in Koc values is still great depending on the soils used in determining the Kd. For example, in Maund et al., (2002) for the 8 replicates tested the cypermethrin mean Koc values were 238,000 (standard deviation [SD] = 38,000; coefficient of variation [CV] = 16%), 502,000 (SD = 27,000; CV = 5%), and 177,000 (SD = 40,000; CV = 23%) for the 1, 3, and 13% OC sediments, respectively. These data suggests significant variation in pore water concentrations for a given contaminant sediment loading, even when normalized for OC. Consequently, more studies are needed to adequately characterize the relationship between the total sediment loading and the bioavailable fraction to sediment-dwelling aquatic life as estimated by the sediment OC content and the Koc. For example, in the analytical methods section of Amweg and Reston (2005) there is the following statement to explain low recoveries "Though the recoveries among sediments were relatively similar for any given compound, Pacheco Creek sediment consistently had the lowest value of the three sediments. This sediment was atypical in that it contained a large proportion of cow manure from surrounding rangeland, raising the possibility that matrix effects may have reduced extraction efficiency." Use of an "atypical sediment" (1 of 3) to derive a sediment chemistry numeric target may not be appropriate.

2) Source Analysis

Section 4 of the Santa Maria Watershed TMDL Final Project Report describes pesticide source analysis. Source analysis is based, in part, on findings of the study conducted by UC Davis that confirmed the association of unknown toxicity to currently applied pesticides (Phillips, 2010). The procedures used to indentify pesticides most likely contributing to water and sediment toxicity are considered current, highly relevant, and comprehensive. Those current use pesticides (OPs and synthetic pyrethroids) for which numeric targets are proposed are listed above. The California pesticide use reporting system is unique, and with the exception of urban use, has provided valuable information on pesticide use in the Santa Maria Watershed. Consultation with local UC Extension has allowed comparison of pesticide use data with cropping practices and pest pressure to construct likely pesticide use patterns in space and time. In the absence of urban pesticide use reporting, procedures described to estimate pesticide use patterns in urban areas are considered thorough and comprehensive, within the limits of the available data and its quality. In addition, the discussion of source analysis of OC pesticide pollution provides a comprehensive outline of the history of OC use, both in agriculture and for mosquito control. However, a discussion of the development of pest resistance to the OCs which resulted in label changes allowing significant increase in application rates and frequency might also be of interest.